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Conformations and mobility of polyethylene and *trans*-polyacethylene chains confined in α-cyclodextrins channels*

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Abstract

Conformational properties and mobility of two polymeric chains containing 30 repeating units of either polyethylene (PE) or *trans*-polyacethylene (PA) confined into the channel formed by eight α-cyclodextrins (αCDs) are studied by Molecular Dynamics simulations performed at 500 K and compared with the behavior exhibited by the same chains when they stand alone in vacuum. The rotaxane structure (i.e. polymeric chains threaded into the αCDs channel) is stabilized with respect to the separated chain and αCDs mostly because of van der Waals interactions. As it might be expected, large differences are observed in the molecular characteristics of the isolated chains as compared to their confined counterparts. The differences are in the sense of decreasing the conformational mobility in favor of extended conformations in the case of confined chains. Comparison of the results obtained for confined PE and PA chains indicates a noticeably larger mobility of the PA chain. Molecular dimensions obtained for the isolated PE chain agree with the results published in the literature.

Keywords

Polyethylene; Cyclodextrin; Polyrotaxane

1. Introduction

A lot of effort is being dedicated nowadays to the study, both with theoretical and experimental approaches of relatively short polymeric chains confined into narrow channels formed by piling up several cyclic molecules. This kind of supramolecular assemble is usually named polyrotaxanes. There are many publications dealing with experimental preparation and characterization of a wide variety of polyrotaxanes including the exploration of several areas of potential utilization [1]; [2] ; [3]. From a theoretical point of view, the two more important questions in the study of polyrotaxanes, are concerned with the rationalization of the driving force responsible for such a supramolecular ordered arrangement and the analysis of the mobility of the polymeric chain threaded into the channel.

Molecular Dynamic (MD) procedures offer very powerful tools to analyze both the energy and geometry of the system under study as it evolves with time. Therefore, it is not just

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by coincidence that MD approaches have been so often employed in theoretical studies of polyrotaxanes. Thus, to name just a few examples, MD simulations have been employed to study paraffins threaded into the *n*-alkane/urea clathrate and polyethylene (PE) confined into the channel of urea [4]. Oligomers of PE [5] ; [6], poly(1,4-*trans*-butadiene) [7]; [8] ; [9] and poly(1,4-*trans*-isoprene) [10] inside the channel of crystalline perhydrotriphenylene have also been studied with this approach.

We have reported MD simulations of polyrotaxanes formed by poly(ethylene glycol) [11] and poly(oxytrimethylene) [12] with α-cyclodextrins (αCDs) and poly(propylene glycol) with β-cyclodextrins (βCDs) [13]. Our main concern in these papers was to determine the stability and configurations of the whole polyrotaxanes, paying less attention to the dynamics of the internal chains. In the present paper we report a MD analysis of two different rotaxanes formed with αCD threaded by a short chain of PE, in one case and of *trans*-polyacethylene (PA), in the other one. The goal of the analysis is also slightly different from the previous one. Thus, in the present case, a detailed description of the mobility of the polymeric chains confined into the channel is obtained and compared with the results obtained, with the same MD strategy, for PE and PA chains standing alone in vacuum and therefore having no steric restrictions imposed by any supramolecular arrangement.

2. Methodology for the molecular dynamics simulations

Molecular dynamics simulations were carried out using the Sybyl molecular modeling package [14] and the Tripos Force Field [15]. The polymeric chains were oligomers containing 30 repeating units of either PE or *trans*-PA that were studied both isolated in vacuum and confined within the channel formed by eight αCDs. The carbon atoms of both chains were sequentially numbered from 1 to 60 and the C–C bonds from 1 to 59. The rotational angle over bond *i* is represented by $_i$ that was taken to be 0 for *trans* orientation. As in our previous papers [11]; [12] ; [13], CDs were oriented head-to-head and tail-to-tail in order to obtain more stability in the complexes. The isolated polymeric chains were abbreviated as PE and PA while RPE and RPA represent their respective polyrotaxanes (i.e. chain plus CDs).

The potential energy of each system *E*, was calculated as a sum of six contributions:

$$E = E_{str} + E_{ang} + E_{tor} + E_{vdW} + E_{elec} + E_{oop} \quad (1)$$

where the terms on the right hand side represent the contributions from bond stretching, bond angle bending, torsion, van der Waals, electrostatic interactions and out of plane potentials. Electrostatics contributions were evaluated using pairwise interactions among partial charges assigned to each atom on the system with a distance dependent effective dielectric constant. Partial charges for PA and PE were computed with MOPAC-AM1) [16] on a tetramer of each polymer chain. Table 1summarizes the charges and geometry employed in this work for ethylene and acethylene units. Geometry and partial charges for αCD were taken from our previous works [11]; [12]; [13] ; [17].

Table 1.
Length, angles, and partial charges in the PE and PA polymer chains

Compound	Bond	Length (Å)	Bonds	Angle (deg)	Atom	Charge (ecu)
PE	C–C	1.552	C–C–C	110.82	C	−0.161
					H	0.081
PA	C–C	1.475	C C–C	122.0	C	−0.128
	C C	1.338			H	0.128

The polymeric chains were initially generated in their all-*trans* conformations. These initial structures were then optimized by conformational energy minimization over all the internal coordinates achieved by means of a simplex algorithm [18] ; [19] followed by a conjugated gradient procedure with a tolerance of 0.2 kcal mol^{-1} $Å^{-1}$ for the rms gradient. The optimized conformations were employed as starting point for all the MD simulations performed with the isolated PE and PA chains.

The undistorted conformation previously described [17] was employed as initial structure of the αCDs. In this conformation, φ (at C(4)–C(1)–O–C(4′)) and ψ (at C(1)–O–C(4′)–C(1′)) torsions at the bridging oxygen were placed at 0 and −3° respectively; the χ (at C(4)–C(5)–C(6)–O) torsions were set to their *trans* state, and the τ bond angle at the bridging O atom was taken to be 130.3°. Two αCDs having this undistorted conformation were then aligned head-to-head (TH–HT) and their structure optimized as function of the distance d between the centers of mass of their six glycosidic oxygen atoms, (C and C′), and their relative orientation, given by the dihedral angle θ formed by O–C–C′–O′. The optimization was performed by moving d within the range 5–12 Å with 0.5 Å increments and θ from 0 to 55° with 5° increments and minimizing the energy at each point with the same scheme described above for the polymeric chains. The best structure thus found has $d = 9.14$ Å, θ=37.6°. The same procedure applied to a pair of αCDs having tail-to-tail (HT–TH) alignment gives d=7.66, θ=47.2°. The starting conformations for the MD simulations of polyrotaxanes was then obtained by aligning eight αCDs in [TH]–[HT]–[TH]– –[TH] sequence and threading the all-*trans* conformation of their respective polymeric chain into the six fold rotation axis of the channel thus formed.

Two sets of MD simulations were performed on polyrotaxanes. In the first set, whose results will be labeled as RPES and RPAS, the conformations of the eight αCDs were kept fixed in their initial (optimized) structure during the whole MD simulation. PE and PA chains were thus allowed to move within a rigid channel. No unthreading of the polymeric chains out of the channel was observed in this kind of simulations.

In the other set that will be represented by RPE and RPA, both the αCDs and the polymer chain are mobile during the MD simulations. In this case, the chains tend to unthread out of the channel. In order to avoid this effect, fluctuations of the distance d from the center of the CD placed at the ends of the channel to the C atom on the polymer chain closest to that center were restricted to the range $d_{ini} \pm 1.0$ Å, with d_{ini} being the value in the initial conformation, by means of a penalty function potential incorporated to the system as an harmonic term $E_p=k(d-d_{ini})^2$ added to Eq. (1). The force constant k was set equal to zero when $(d - d_{ini})^2 \leq 1.0$ Å and to 200 kcal mol^{-1} Å^{-2} otherwise.

All the MD simulations were performed by means of the Verlet algorithm [20] with a time step of 2 fs. Atomic velocities were rescaled and linear and angular momentum of the entire system removed at intervals of 10 fs. Bonds connected to hydrogen atoms were constrained in their unstressed lengths during all the MD simulations. However, all other bonds lengths, bond angles and torsions were allowed to fluctuate. The first part of the simulations was a thermostationary process during which the system was heated up from 0 to 500 K with 10 K increments and allowing 300 fs for equilibration after each increment. Once the system reached the final working temperature of 500 K, it was allowed to equilibrate for 0.1 ns. After this preparation, the data collecting stage was initiated. It consisted of an additional simulation of 1 ns during which the conformation of the system was saved with 200 fs intervals thus providing 5000 images for subsequent analysis.

The binding energy of the system ($E_{binding}$), defined as the non-bonded interaction between the polymer chain and the CDs in the polyrotaxanes, was evaluated for each image as the difference between the total energy of the rotaxane and the sum of the energy of the polymer chain plus the CDs:

$$E_{binding} = E_{polyrotaxane} - (E_{polymer} + E_{CDs}) \quad (2)$$

and the average of any property $\langle X \rangle$ was obtained as,

$$\langle X \rangle = \frac{1}{N} \sum_{i=1}^{N} X_i \quad (3)$$

where N=5000 is the number of images and X_i is the value of the property for the image i.

3. Results and discussion

3.1. Stabilization of the polyrotaxanes

The $E_{binding}$ and its components for all polyrotaxanes are collected in Table 2. All polyrotaxanes have negative $E_{binding}$ values. The van der Waals interactions are the main contribution to the $E_{binding}$ for the stabilization of the complex by more than 99%. These results agree with other works on PEG:αCD [11], POT:αCD [12] and PPT:βCD [13] polyrotaxanes. Fig. 1depicts the conformation of minimum potential energy for RPAS and RPES simulations. It shows that most of the bonds on the internal chains are in the *trans* state.

Table 2.
Binding energy together with van der Waals and electrostatic contributions for the polyrotaxanes studied. Units of kcal mol^{-1}

Compound	$E_{binding}$ (total)	$E_{binding}$ (van der Waals)	$E_{binding}$ (electrostatics)
RPE	−136.4	−133.8	−2.7
RPES	−150.5	−148.3	−2.2
RPA	−137.0	−127.2	−9.8
RPAS	−118.3	−117.4	−1.1

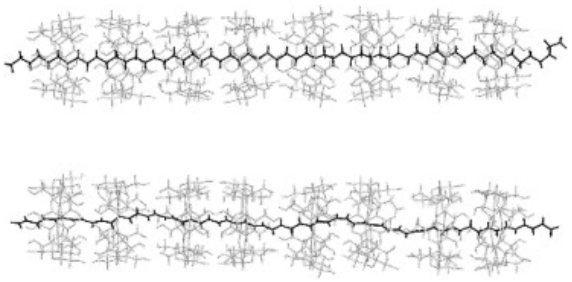

Fig. 1.
Conformations of minimum potential energy for RPES and RPAS obtained during MD simulations of 1 ns at 500 K.

According to the results shown in the second column of Table 2, the PE rotaxane is more stable than its PA counterpart when the CD's channel is kept immobile. Thus, RPES exhibits larger negative value of $E_{binding}$ than RPAS. This difference may be due to the smaller molecular volume of the PA chain as compared to PE (after all, the –CH CH– repeat unit contains two atoms less than $–CH_2–CH_2–$) that allows larger mobility of the PA chain than its PE counterpart when they are both within the CD's channel (see below). Thus, while the PE chain will find the most stable conformation relative to the CD's channel and remain practically immobile during the MD trajectory, the PA chain rotates passing through several energy minima, but also through some maxima so that the average energy becomes higher. However, when the CD's channel is allowed to fluctuate, both rotaxanes have practically the same value of $E_{binding}$ since the differences shown in Table 2 between the values for RPE and RPA are within the limit of accuracy of the calculation. It seems that, in these cases, the distortion of the polymeric chains and the CD's channel couple themselves in the sense of achieving the most stable conformation and the possible increase of energy necessary to produce larger distortions that will be required to fit two extra H atoms in the PE chain as compared to PA is almost exactly counterweighted by the attraction that those two atoms produce in the most stable conformation.

3.2. Conformational analysis of the polymer chains

The skeletal bonds in the isolated PE chain visit the three classical states; *trans* (T), *gauche*$^+$ and *gauche*$^-$ ($G^{\pm}$). However, the single bonds of PA prefers *trans* (T) and two skew states $S^{\pm}$ separated ca. ±30° from *cis*. Alternate double bonds of PA chains obviously always populate T states and only small fluctuations around these states are observed during the MD trajectory.

For the purpose of classification of the rotational states of the CH_2–CH_2 bonds in PE we use $-60° \leq \phi_i \leq 60°$ for a T state, $60° < \phi_i < 180°$ for G^+ and $-180° < \phi_i < -60°$ for G^-. In the case of PA chains, the classification of states is $-90° \leq \phi_i \leq 90°$ for T, $90° < \phi_i < 180°$ for S^+ and $-180° < \phi_i < -90°$ for S^- states.

Fig. 2depicts the probability of *trans* (T) states at each skeletal bond from 2 to 58 for all the systems studied here, namely: isolated PE and PA chains and polyrotaxanes having the CD channel either mobile (RPE and RPA) or fixed (RPES and RPAS). In the case of PA chains, only single bonds, labeled as odd, are depicted. All bonds (apart from the ones placed close to both ends and some exceptions in RPAS) have a higher population of T states in the polyrotaxanes than in their free polymer chains counterparts.

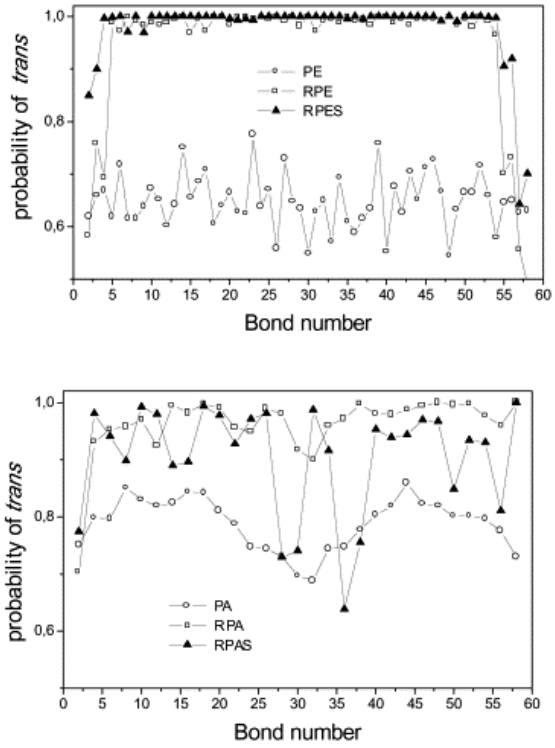

Fig. 2.
Probability of T states for each skeletal bond of all the polymer chains studied.

Population of T states for all the studied chains were averaged over the 20 central repeating units, i.e. disregarding five units at each extreme in order to avoid end effects. The results are represented in Fig. 3and summarized in a more quantitative way in the second column of Table 3. Both of them illustrate the same main feature: The chains exhibit a larger preference for T, and consequently are much more extended, when confined into the αCDs channel than in their isolated state. It is interesting to notice that our results for PE isolated chains are in good agreement with those reported by Abe et al. [21] whose rotational isomeric state model provides a fraction of 0.6 for *trans* states and averaged values of $\langle \phi_i \rangle = 0, \pm 112.5°$ for T and $G^{\pm}$.

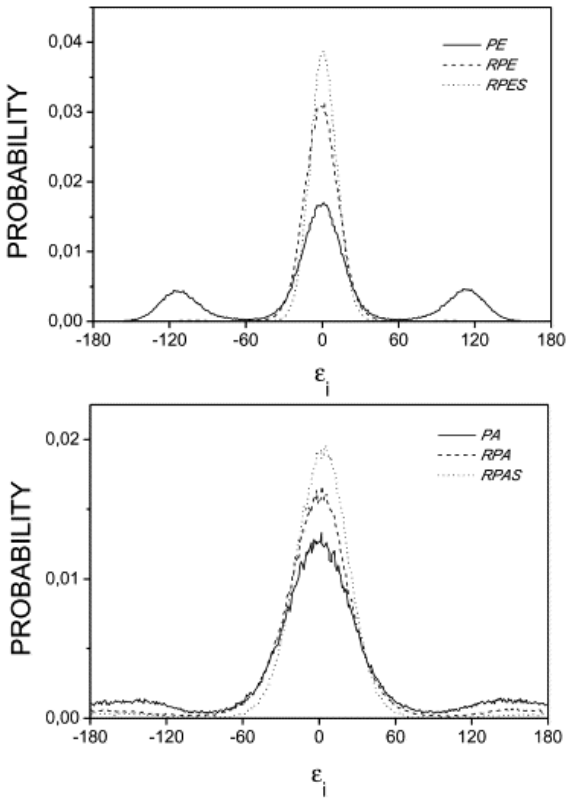

Fig. 3.
Averaged probability distributions for the rotational angles $_i$ over each single skeletal bond of all the polymer chains studied. Individual values were computed by means of a 1 ns MD simulation at 500 K and then averaged for the 20 central repeating units of each chain, thus disregarding 5 units at each extreme in order to avoid end effects.

Table 3.
Conformational properties (% of *trans* states and fluctuations $\delta|\ -\ _{trans}|$ for skeletal single bonds) and molecular dimensions (end-to-end distance, radius of gyration and characteristics ratios) for all the polymeric chains studied. Averages were performed over the 20 central repeating units of the isolated chains (PE and PA) and polyrotaxanes (RPE, RPES, RPA and RPAS). Standard deviations are in parenthesis

Compound	% $_{trans}$	$\delta\|\ -\ _{trans}\|$	$\langle r^2\rangle^{1/2}$ (Å)	$\langle s^2\rangle^{1/2}$ (Å)	C_{40}
PE	64.9 (5.7)	47.3 (5.6)	21.4	8.9	4.8
RPE	99.2 (0.8)	11.2 (2.9)	54.7	16.3	31.1
RPES	99.9 (0.3)	7.1 (1.8)	54.8	16.2	31.2
PA	78.6 (5.0)	47.4 (2.9)	29.2	11.3	10.7
RPA	97.1 (2.9)	20.6 (9.7)	50.9	15.3	32.7
RPAS	90.3 (10.6)	30.5 (14.4)	52.2	15.4	34.3

Table 4collects the probabilities for the nine combinations of conformational states of consecutive pairs of bonds for all the chains. Results of Table 4 reveal the well-known behavior of unperturbed PE chains [21], namely that TT pairs are the most important states followed by the four $G^{\pm}T$ and $TG^{\pm}$ combinations. $G^{\pm}G^{\pm}$ pairs are less populated and finally $G^{\pm}G$ combinations are almost negligible due to a strong second-order repulsion. The TT sequence is also the preferred on in the case of PA chains (either free or in the complex) while none of the SS pairs is allowed due to the alternation of single/double bonds. Obviously, the preference for TT states is stronger in the complexes. Similar calculations performed of triads of consecutive bonds, and not summarized here, reveal that the most favorable triplets in isolated chains are TTT and the preference is increased in the complexes, especially for RPES whose chain bond rotations are almost hindered. Triplets with sequences in which two T states are present are also highly probable.

Table 4.
Probabilities of conformational states for consecutive pairs of bonds for the 20 central monomer units of

the isolated chains (PE and PA) and polyrotaxanes (RPE, RPES, RPA and RPAS). X means G (or S) states for PE (or PA) chains

Pairs	PE	RPE	RPES	PA	RPA	RPAS
TT	0.398	0.984	0.997	0.830	0.952	0.929
$X^{\pm}T$	0.254	0.007	0.001	0.085	0.011	0.036
$TX^{\pm}$	0.254	0.007	0.001	0.085	0.037	0.036
$X^{\pm}X^{\pm}$	0.072	0	0	0	0	0
$X^{\pm}X$	0.022	0	0	0	0	0

Comparison of the results for both kinds of polyrotaxanes, shown in Fig. 2, also reveal that single internal bonds of RPA and RPAS visit other states different from T more often than RPE and RPES during the 1 ns MD trajectory. Fig. 4depicts the number of transitions between possible states for single bonds of all the chains. These values were evaluated by counting the number of times the value of the $_i$ rotation crossed the boundary between two adjacent states. The number of transitions between S^+, S^- and T states in isolated PA is larger than between G^+, G^- and T states in isolated PE which reveals a smaller energy difference between states in PA than in PE. Obviously, the number of transitions at each single bond is larger for isolated chains than for polyrotaxanes. The smaller molecular volume of the PA chain as compared to PE (see above), also permits more conformational changes of the PA chain inside the CD channel than in the PE counterparts. This fact is more evident for polymer chains inside the rigid CD channel on the RPAS series. The PA chain can change conformations inside the relatively wide fixed CD channel more often than the bulkier PE chain whose movement is more hindered. Table 5collects the average number and type of transitions for the compounds studied.

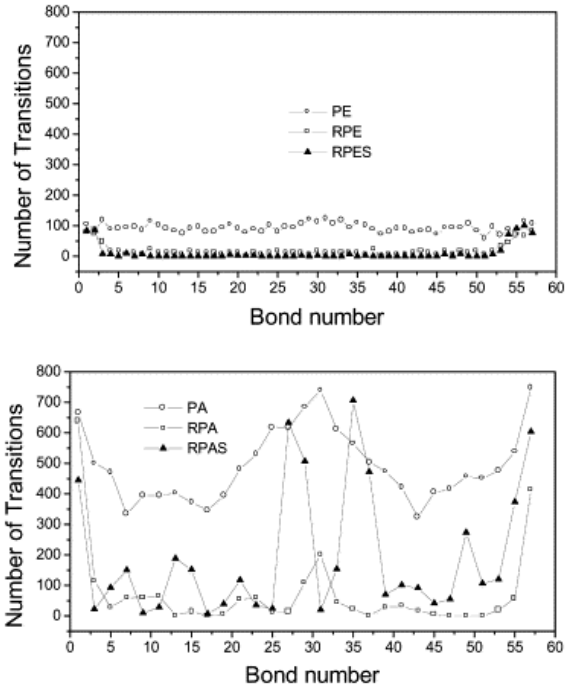

Fig. 4.
Number of transitions between states for each single bond, labeled from 1–59, of the polymer chains studied.

Table 5.
Averaged number of transition between states allowed to the single bonds for the 20 central monomer units of the isolated chains (PE and PA) and polyrotaxanes (RPE, RPES, RPA and RPAS). Standard deviations are in parenthesis. X denotes G or S states for PE and PA chains respectively

Compound	$X^+ \leftrightarrow X^-$	$X^- \leftrightarrow T$	$X^+ \leftrightarrow T$
PE	1.5 (1.5)	47 (10)	45 (10)
RPE	0 (0)	5 (3)	6 (4)

RPES	0 (0)	0 (0)	1 (2)
PA	187 (32)	145 (43)	157 (56)
RPA	25 (47)	7 (7)	5 (5)
RPAS	98 (152)	47 (78)	35 (35)

The fluctuation in the *trans* state can also be a quantitative measure of the conformational changes of the polymer chain. This magnitude is defined for bond *i* as:

$$\delta|\epsilon_i - \epsilon_{trans}| = [\langle|\epsilon_i - \epsilon_{trans}|^2\rangle - \langle|\epsilon_i - \epsilon_{trans}|\rangle^2]^{1/2} \quad (4)$$

where $_i$ represents the value of the rotational angle at a given moment (i.e. in one of the images of the system collected along the MD trajectory), $_{trans}$=0 is the main value for a T state and the angular brackets denote the average over the whole simulation. The third column on Table 3 collects the average of this magnitude for all internal single bonds on the 20 central units of each chain. As expected, values of this fluctuation are larger for isolated chains than for polymer chains confined into the complex where their mobility is severely restricted. There are also differences between PE and PA complexes. Larger values for the PA complexes reveal larger conformational mobility of the PA chain inside the cavity as compared to PE.

The end-to-end distance and the radius of gyration for the central 20 repeating units were also calculated for all the chains and their values are collected in columns four and five of Table 3. As it is apparent from Table 3, all polyrotaxanes have larger values for both magnitudes than their corresponding free polymer chains. On the other hand, the free PA also has larger values than the free PE. These results agree with the larger population of T states for polyrotaxanes as compared to the free PE and PA polymer chains and also for the free PA as opposed to the free PE. The last column on Table 3 shows the characteristic ratios defined as $C_n = \langle r^2 \rangle / nl^2$, with n=40 skeletal bonds in this case. Our result of 4.8 for the isolated PE chain is slightly smaller than those of C_∞ experimentally obtained [22] or calculated [21] ; [23] that are in the range 5.2–7.0, although it should be taken into account that our chains are rather short and C_n probably has not yet reached the asymptotic C_∞ limit.

It is interesting to note that, according to all the results indicated above, the PA chain is more rigid and more extended than the PE one when they are both in isolated (higher % of *trans* state and molecular dimensions). However, the situation reverses and PE becomes more rigid and more extended than PA when they are both threaded into the αCDs channel. In the case of PE, the fact of having flexible (i.e. RPE) or rigid (i.e. RPES) channel has no incidence on the conformational properties of the chain. However, the inner chain on RPAS (rigid channel) has a larger preference for *trans* than its RPA (flexible channel) counterpart, although its effect on the chain dimension is negligible.

3.3. Mobility of polymer chains within the CDs crystalline channel

The mobility of the polymeric chains confined within the αCDs channel was analyzed for the RPAS and RPES series, i.e. with the channel keeping its initial, minimum potential energy conformation during the whole simulation. The coordinate system employed for this analysis was affixed to the channel. The origin was placed at the center of mass of the bridging oxygen atoms on the first CD unit. The *z* axis follows the direction of the six-fold rotation axis of this CD. The *y* axis passes through one of six bridging oxygens of the first CD. Finally, the *x* axis completes a right-handed frame. The movement of the polymeric chain could then be studied by analyzing the time evolution of the position of some selected atoms relative to that motionless frame.

3.3.1. Mobility of the carbon atoms

The eight C atoms occupying positions 5, 10,…, 45 in the polymeric chains were selected for this study. Fig. 5shows, as an example, the instantaneous *xy* projection of the placements of C(20) and C(25) for PE and PA chains in RPES and RPAS polyrotaxanes. Similar plots were obtained for the other carbon atoms studied. These projections are affected mainly by rotations of the chain as a rigid body within the channel, but they also change by fluctuations and conformational transitions over the

single C–C bonds, and even by fluctuation over T states at the C C bonds in PA. A quantitative description of the amplitude of the oscillations on that projection is afforded by the standard deviation of the average of $(x^2+y^2)^{1/2}$ over the whole MD trajectory of the eight C studied, which amounts to 0.178 Å and 0.330 Å for PE and PA respectively. These results indicate that the mobility due to both the rotation as a body of the whole polymer chain around the *z* axis and the conformational changes (or fluctuations) of the chain within the CDs channel is smaller for PE than for PA. This behavior could be because PE is bulkier than PA is and therefore the free volume within the channel is smaller in RPES than in RPAS.

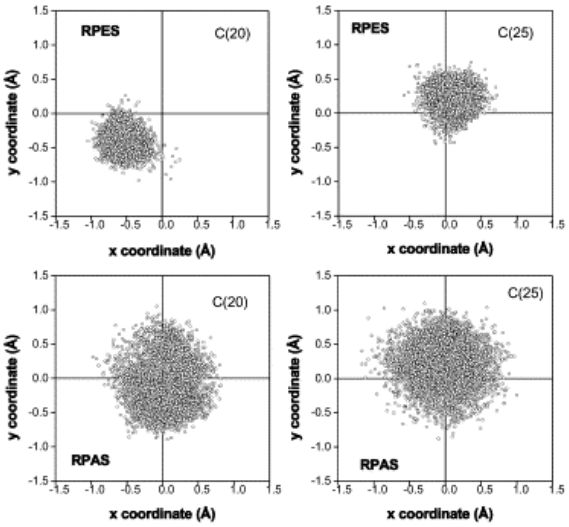

Fig. 5.
Projection over the *xy* plane of the instantaneous position of C(20) and C(25) skeletal atoms of the polymeric chain confined into the αCDs channel. The coordinate system is affixed to the first CD and the *xy* plane is perpendicular to the direction of the channel. Each picture contains 5000 points representing the position occupied by the C atom at intervals of 200 fs during the whole MD trajectory.

Translational movement of the polymer chain inside the CD channel was assessed by measuring the *z* coordinate for each of the carbons studied. Fig. 6depicts plots of *x* vs. *z* and *y* vs. *z* coordinates for the placement of the eight carbon atoms studied for the inner chains of RPES and RPAS complexes. As Fig. 6 indicates, both PE and PA polymer chains hardly move along the *z* axis within the rigid channel.

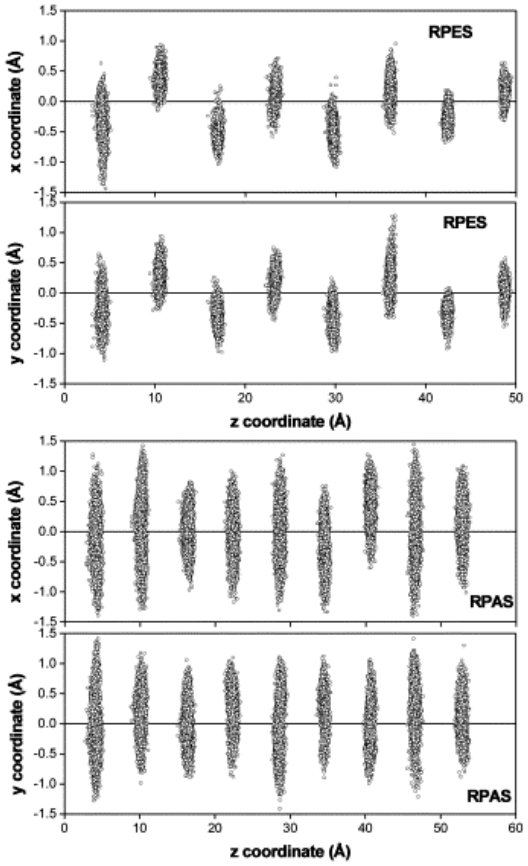

Fig. 6.
Plots of *x* vs. *z* and *y* vs. *z* coordinates for the placement of the eight carbon atoms studied in the inner chain of RPES and RPAS complexes.

3.3.2. Mobility of the hydrogen atoms

The H atoms attached to the same C atoms selected in Section 3.3.1 were chosen for this analysis. Fig. 7shows, as an example, the *xy* projection of the instantaneous position of H atoms bonded to C(20) and C(25) on the PA (one H per C) and PE (two H per C) polymer chains inside channel. The H atoms of both chains fluctuate around equilibrium positions. However, they are distributed over a much wider region in PA than in PE. The conclusion is similar to the one described in Section 3.3.1: The mobility of hydrogen atoms is larger in the case of PA than in PE.

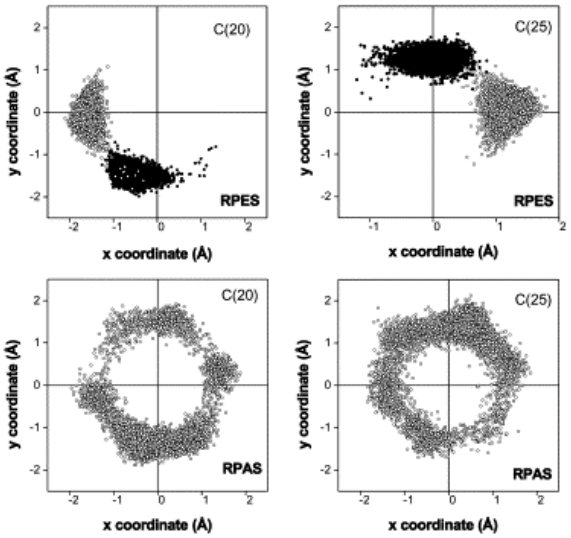

Fig. 7.
Instantaneous projection over the *xy* plane of the placement of H atom (PA chains) or two atoms (for PE) bonded to C(20) and C(25) skeletal atoms of the inner chains of RPES and RPAS. Open and solid shots on top are used to distinguish positions of each of the two H atom in PE. See text and legend for

Fig. 5 for details.

3.3.3. Rate of rotation around the *z* axis

One method for detecting this motion is the analysis of the time dependence of $\langle\psi\rangle_t$. Let $\psi(t,j)$ denote the angle between the *x* axis and the projection over the *xy* plane of the vector defining the position at time *t* of an H atom bonded to *C*(*j*) of the polymeric chains in RPES and RPAS complexes. Assuming that we select *M* such atoms and compute the average:

$$\langle\psi\rangle_t = \frac{1}{M}\sum_{j=1}^{M}\psi(t,j) \tag{5}$$

in total absence of conformational changes, this average would be sensitive to the rotation of the whole chain as a rigid body. This is almost true for RPES complexes, where the number of T↔G± transitions is considerably low.

The initial value $\psi(t=0,j)$ was taken as reference for each projection by subtracting that value from the results $\psi(t,j)$ obtained at $t>0$. Therefore, $\langle\psi\rangle_{t=0}=0$. However, the sign of each projection was retained for the analysis, so that right-handed and left-handed rotations are distinguished.

Calculations were performed selecting *M*=40 H atoms on each polymeric chain. In the case of PA they were those attached to C atoms within the 20 central repeating units, i.e. C(6) to C(25). In the PE however, only one H per C from C(6) to C(25) was selected in such a way that their position alternate above/below the plane of the backbone when the chain is in the all-*trans* conformation. The results are shown in Fig. 8, which indicate that the PE chain hardly rotates within the CD channel. It just fluctuates around the T states and, after approximately 0.25 ns, experiences a small rotation of a few degrees to the right, keeping this orientation during the rest of the trajectory. The PA chain however presents values of $\langle\psi\rangle_t$ in the range of approximately −100 to +300°. The chain initially rotates slightly to the left and after approximately 50 ps experiences a rotation of 300 degrees to the right in the next 0.2 ns and then the same degrees to the left up to reach 0.42 ns of the trajectory. Then, again 300 degrees to the right in the next 0.2 ns. For the last 200 ps, the molecule rotates more than one revolution to the left. This result demonstrates that the PA chain is more mobile in the CD channel than the PE one. However, conformational changes instead of rotation of the whole chain as a body may be responsible of this mobility.

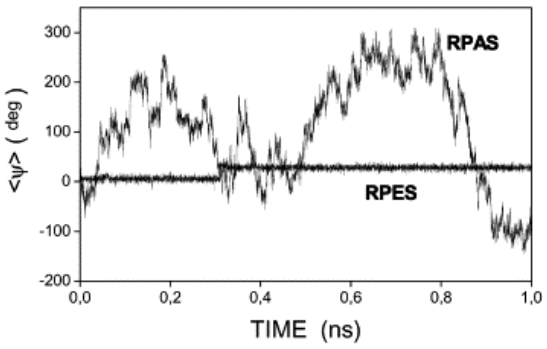

Fig. 8.
History of $\langle\psi\rangle$ over 1 ns MD trajectory at 500 K for the inner chains in RPES and RPAS complexes.

The instantaneous rotational rate at time *t* can be defined as

$$\frac{\partial\psi}{\partial t} \approx \frac{\Delta\psi}{\Delta t} = \frac{|\langle\psi\rangle_t - \langle\psi\rangle_{t-\Delta t}|}{\Delta t} \tag{6}$$

where Δt is the interval at which the trajectory was recorded for subsequent analysis (200 fs in the present case). The average rotational rate is identified with the simple average of the 4999 successive values of the instantaneous rate, using the 4999

successive records separated by Δt. This average is abbreviated as $\langle|\Delta\psi|\rangle/\Delta t$. The values of $\langle|\Delta\psi|\rangle/\Delta t$ extracted from the 1 ns trajectories are 27.2 and 50.0 deg ps^{-1} for PE and PA, respectively.

3.3.4. Influence of changes and/or fluctuation at the internal dihedral angles

The previous analysis does not distinguish between rotations of the whole chain as a body and conformational changes and/or fluctuation at the internal single bonds of the polymer chains, especially for PA chains whose conformational changes are considerable. In order to assess the importance of this fact, let $\varphi(t,j)$ denote the instantaneous value at time t of the dihedral angle at the jth internal single bonds for the 20 central monomer units of PA and PE. The average value of $\varphi(t,j)$ for M dihedral angles at time t is:

$$\langle\phi\rangle_t = \frac{1}{M}\sum_{j=1}^{M}\phi(t,j) \tag{7}$$

The instantaneous rate of variation at time t is:

$$\frac{\partial\phi}{\partial t} \approx \frac{\Delta\phi}{\Delta t} = \frac{|\langle\phi\rangle_t - \langle\phi\rangle_{t-\Delta t}|}{\Delta t} \tag{8}$$

and the average over 4999 values, separated by $\Delta t = 200$ fs, is denoted by $\langle|\Delta\varphi|\rangle/\Delta t$.

If the whole polymer chain rotates as a body inside the channel (i.e. either conformational changes do not take place or there is a compensation among conformational changes of different bonds along the chain), $\langle\varphi\rangle_t$ should be zero during the whole MD trajectory and its average, given by Eq. (8), would also vanish.

Fig. 9depicts the history of $\langle\varphi\rangle_t$ for RPES and RPAS complexes over the 1 ns trajectory. Averaging of these results over time provides $\langle|\Delta\varphi|\rangle/\Delta t$=3.0 and 4.2 deg ps^{-1} respectively for the PE and PA chains inside the CD channel. The same calculation performed for isolated PE and PA chains yields $\langle|\Delta\varphi|\rangle/\Delta t$=6.3 and 28.0 deg ps^{-1} respectively. These results indicate, once again, that the conformational mobility of the polymeric chains is smaller when they are confined into the αCD channel than in their isolated state. Nevertheless conformational changes and fluctuations are important enough in the case of PA as to produce a left-hand rotation of the whole chain that amounts to ca. 90 deg after 1 ns.

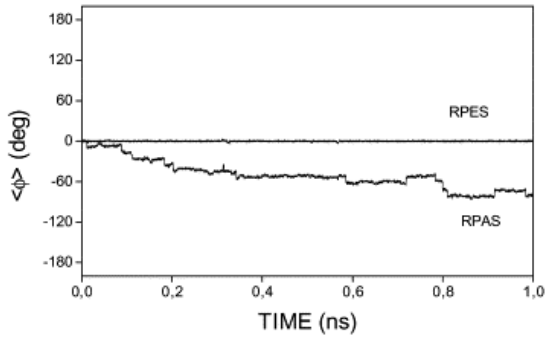

Fig. 9.
History of $\langle\varphi\rangle_t$ under the same conditions as Fig. 8.

Comparison of these values of $\langle|\Delta\varphi|\rangle/\Delta t$ with their corresponding ones for $\langle|\psi|\rangle/\Delta t$ indicates that the former magnitude amounts only to ca. 11 and 8% of the latter one respectively for RPES and RPAS. Taking into account that both conformational changes (or fluctuations) and rotation of the whole chain contribute to the value of $\langle|\psi|\rangle/\Delta t$ while $\langle|\Delta\varphi|\rangle/\Delta t$ is only due conformational changes or fluctuations, the results at hand suggest that this last kind of processes does not make an important contribution to the relatively rapid orientation of the xy plane projection of the origin-H bond vectors. This fact is quite apparent for RPES where the population of T states is almost 100% and only fluctuations around this state, with relatively low rate, are

allowed. However, conformational changes take place for PA chains confined into the CD channel that produce a slight rotation (with low rate) of the chain to the left, in the direction opposite to the rotation of origin-H vectors. Therefore, we conclude that while the PE chain is almost immobile within the CD channel, a slight rotation of the whole chain of PA as a body takes place during the MD trajectory of 1 ns at 500 K.

3.3.5. Translation of the chain along its long axis

Let $Z(t,j)$ denote the instantaneous value at time t of the z coordinate on atom j and Z_t the average over several atoms on the chain, for instance over all C atoms or over all H atoms. The instantaneous rate of translation was defined as:

$$\frac{\partial Z}{\partial t} \approx \frac{\Delta Z}{\Delta t} = \frac{|Z_t - Z_{t-\Delta t}|}{\Delta t} \tag{9}$$

and the simple average obtained from 4999 evaluations separated in time by $\Delta t = 200$ fs is denoted by $\langle|\Delta Z|\rangle/\Delta t$.

The average rate of translational motion for the carbon atoms was found to be 0.93 and 0.96 Å ps^{-1} respectively for PE and PA within their corresponding RPES and RPAS complexes. The value of the same magnitude for hydrogen atoms is 1.15 and 1.2 Å ps^{-1}. These results are very similar and prove that the Z translation of chains inside the channel is not very important.

4. Conclusions

From our results we can conclude that polyrotaxanes formed by polymeric chains of PE and PA confined into channels of αCDs are stabilized with respect to systems formed by separated, non interacting polymeric chains plus αCDs. Van der Waals interactions between the polymeric chain and the αCDs are responsible for ca. 99% of this stabilization. The same effect has been found in other polyrotaxanes [11]; [12] ; [13].

The *trans* state is strongly preferred at all internal bonds of both the PE and PA chains confined within the αCDs channel, causing them to become much more extended than their free polymer chain counterparts. The results of several magnitudes such as the probability distribution of states, end-to-end distance, radius of gyration, characteristics ratio, etc. corroborate this last conclusion.

The analysis of the MD trajectories shows that the movement of the carbon and hydrogen atoms inside the channel is much larger for PA than for PE. The larger volume of the PE chain as compared to the PA one makes the PE chain hardier to move from the initial all *trans* conformation. The simulation also reveals contributions to the dynamics of the PA chain due to both the rotation of the whole chain as a rigid body about its long axis and the conformational changes over internal single bonds, although the former contribution is by far the most important one.

Translation of the chain along the 6-fold αCDs axis (z axis) is negligible in the polyrotaxanes studied.

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